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QUANTUM MECHANICS APPLIED TO DYE LASERS

by

Carol K. Pearce

September 1981

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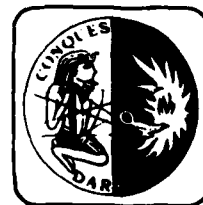**NIGHT VISION & ELECTRO-OPTICS LABORATORY**
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The application of quantum mechanics to dye laser theory is reviewed, based upon recent semiclassical and fully quantum mechanical studies. Both semiclassical and fully quantum mechanical approaches were included. Phenomena investigated in the dye laser medium included spectral hole burning, propagation of light pulses, and light absorption and emission. Some studies realistically included consideration of the triplet state. Mixtures of lasing dyes, or of lasing and saturable absorber dyes, were not treated, nor were vapor dye lasers. Theoretical limitations that might be inherent in dye lasers, such as gain and power output, are other important areas that deserve examination in future studies.

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# QUANTUM MECHANICS APPLIED TO DYE LASERS

## I. INTRODUCTION AND BACKGROUND

Successful lasing in an organic dye was not reported until 1966 although the first successful laser was developed in 1961. Use of dyes as saturable absorber laser Q-switches preceded the laser dye success and continues to the present. NV&EOL has successfully applied the incorporation of a dye Q-switch in low-energy laser rangefinding systems. High-energy applications were explored. A concerted effort was made to extend the long wavelength applicability of the dye Q-switch through the creation of new dyes. A close relationship exists between dye lasers and dye Q-switches. One of the first instances of lasing in a dye occurred inadvertently during a search for new dye Q-switches. Developments in the more widely studied phenomenon of dye lasers support our mission in dye Q-switches and have provided a stimulus for this report.

Both pulsed and continuous wave (CW) dye lasers are operational in configurations much like those used for other lasers (except for modifications required to offset losses due to the triplet state). Numerous organic dyes have been found to lase; the cyanine, coumarin, xanthene, and oxazine classes are of major importance.[1] The tunability inherent in dye lasers is probably their most useful asset. Depending upon the choice of dye, tunable radiation can be generated from the near ultraviolet to the visible and near infrared regions of light. Linewidths as narrow as $10^{-4}$ nanometers are available, as are pulse widths of 0.01 nanosecond duration.[2] When saturable absorber mode locking dyes are incorporated in the laser cavity, picosecond pulsewidths become attainable. Both CW and pulsed (0.1 to over 300 p/s) operation can be obtained commercially, with peak power up to $2 \times 10^6$ watts being cited.[2] Energies between several microjoules and up to over 10 joules per pulse have been reported.[3] The potential of the dye laser in integrated optical elements has been discussed with possible applications in communications and data transmission.[3] The precise tunability of dye lasers mandate their use in spectroscopic studies and in such practical applications as LIDAR. LIDAR (Light Detection and Ranging) enables one to detect and measure trace atmospheric pollutants by a radar type of fluorescence technique.[3] Dye lasers have been investigated for optical warning/detections systems and as human optical countermeasure sources.[4][5] More extensive application of

[1] K. H. Drexhage, "Structure and Properties of Laser Dyes," in "Dye Lasers," Chap. 4, ed. by F. P. Schaefer, Springer-Verlag, New York (1973).

[2] "Laser Focus Buyer's Guide," pp 143-144, Advanced Technology Publications, Inc., Newton, MA (1979).

[3] T. W. Hänsch, "Applications of Dye Lasers," in "Dye Lasers," Chap. 5, ed. by F. P. Schaefer, Springer-Verlag, New York (1973).

[4] L. Gampel, S. Guch, and H. Wang, "Dye Laser Module," U.S. Army Research and Development Report, ECOM 76-1972-1 (Feb 77).

[5] D. H. Sliney and T. L. Lyon, "Evaluation of a Phase-R Dye Laser in Phase II of an ECOM Countermeasure Source Evaluation," AD-917 016L, Defense Documentation Center, Alexandria, VA (December 1973).

the dye laser can be expected in all of these areas, particularly as the state-of-the-art advances. Some of the improvements that should develop are: dyes and host materials designed specifically for dye laser systems, vapor dye lasers operable in the visible and near infrared (and pumped by electrical discharge or electron beam sources, and modifications in the laser module itself.

As dye laser technology requires increasingly unique responses, rather than merely borrowing from the existing technologies of dyes, photochemistry, and lasers, guidance will be needed from theoretical treatments. Much of the theoretical work done on dye lasers is based upon energy balance and rate studies. Quantum mechanical treatments of dye laser systems are, at present, much less numerous than for other laser systems. Among the few quantum mechanical dye laser studies are the semiclassical theories of Eberly, Chin and Zardecki, and Vahey and Yariv.[6][7][8] A fully quantum-mechanical study was reported recently by Schaefer and Willis.[9] The intent of this report is to discuss dye lasers as a case of light interacting with matter, the case being treated quantum mechanically. How quantum mechanics is applied, and the kinds of problems solved, will be of major interest.

Aspects of dye lasers covered in these quantum mechanical treatments to be discussed more fully below, include:

a. Application of the Lamb laser theory to dye lasers.[6]

b. The propagation and superposition of light pulses in a dye-solvent medium.

c. The absorption of light in organic dyes (both in dye lasers and as saturable absorbers) as it is affected by spectral cross-relaxation and collisional dephasing.[8]

d. Development of a completely quantum mechanical theory of dye lasers, including an exact calculation for the dye triplet state.[9]

Basic to all of these studies is the fact that organic dye molecules, upon absorption of light quanta, undergo an optical transition from a ground (singlet) state energy level to a higher excited singlet energy level. Decay to the ground state results in fluorescent emission, comparable to the laser emission when the dye is in a laser cavity. Intersystem crossing (where $k_{ST}$ is the intersystem crossing rate) can easily occur, however, so that the excited singlet may decay instead to a triplet level (Figure 1). Thus the efficiency of the (singlet) emission process is reduced.

[6] J. H. Eberly, "Toward a Theory of the Dye Laser," "Atomic and Molecular Optics," Proc. Rochester Symp., ed. by J. H. Eberly, Univ of Rochester (March 1971); also US Gov't Publication AD725218 (Defense Documentation Ctr), Alexandria, VA.

[7] A. L. Chin and A. Zardecki, Phys. Rev. A, 13, 1528 (1976).

[8] D. W. Vahey and A. Yariv, Phys. Rev. A, 10 (6) 1578 (1974).

[9] R. B. Schaefer and C. R. Willis, Phys. Rev. A, 13 (5) 1874 (1976).
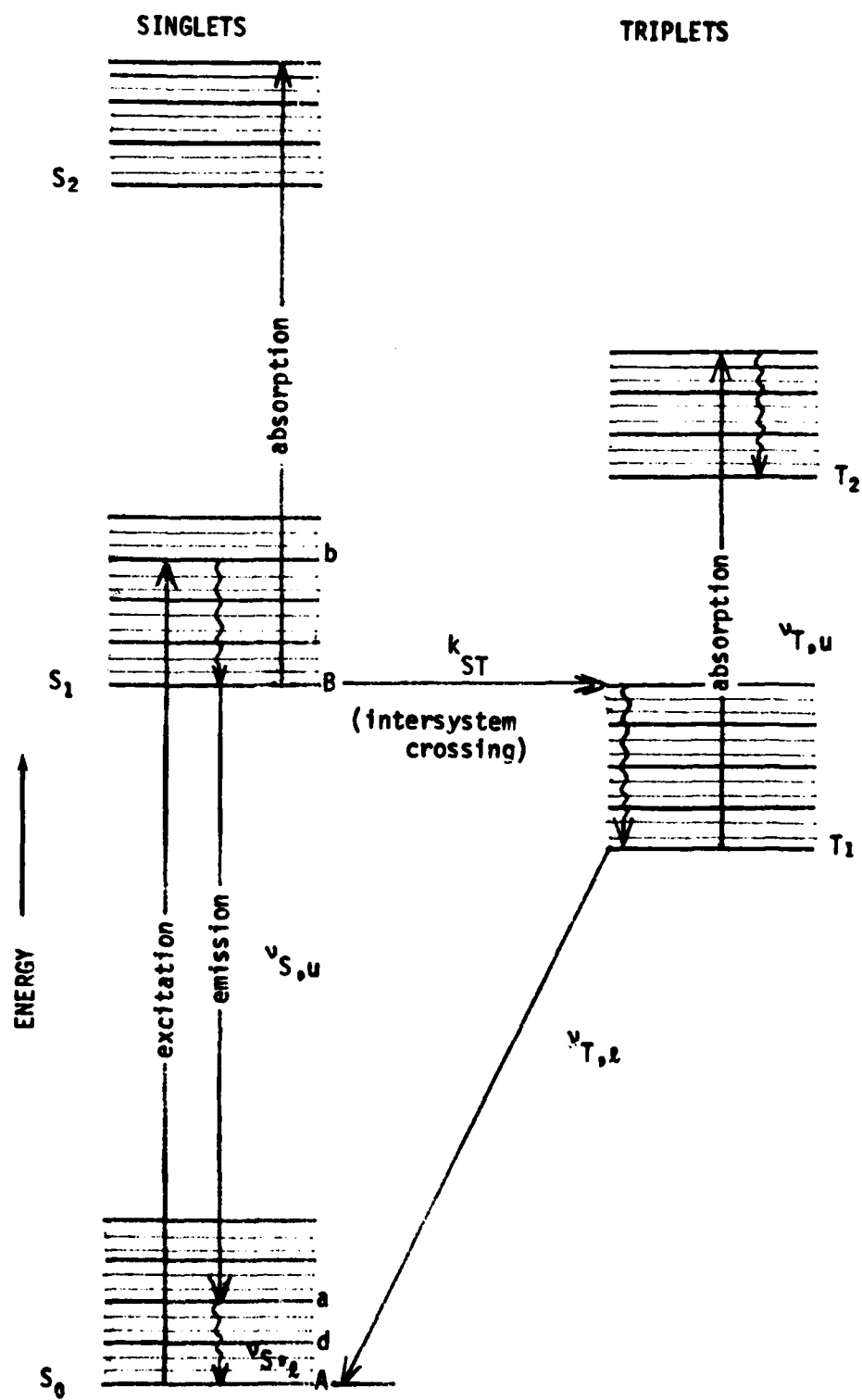
Figure 1. Typical Jablonski energy level diagram for dye molecules.

The distribution of molecules upon interaction with light will be among a minimum of four energy levels, so that the organic dye laser must be considered as a four-level system at least, in contrast to the two-level laser of Lamb's theory.[6] Unlike other laser media, furthermore, organic dyes are characterized by broad absorption and emission bands. These broad bands afford the tunability for which dye lasers are known. They indicate also that many vibrational/rotational levels are populated for a particular electronic transition.

In the discussions to follow, the use of density matrices will be found to be most useful in formulating the equations of motion for dye molecules moving through an electric field (the field due to the electric component of light waves).[10] [11] The density matrix is one whose elements are bilinear combinations of the probability amplitudes, $C_A$ and $C_B$ (if $\psi(r, t)$ is a known wave function):[10]

$$\psi(r, t) = C_A(t)\psi_A(r) + C_B(t)\psi_B(r), \tag{1}$$

where $\psi(r)$ is the stationary, or time-independent, wave function for molecules A or B.

Sargent, Scully, and Lamb (hereafter SS&L) have discussed the above "pure case" as well as the more generally useful "mixed case" when the state vector (in Dirac motion) $|\psi(t)>$ is unknown.[10] The wave function $\psi(r, t)$ is an expansion coefficient of the state vector.[10] Thus, $\varrho$ is the general density operator

$$\varrho = \sum_j P_j |\psi_j><\psi_j|. \tag{2}$$

$P_j$ is a probability factor for systems which have a state vector $|\psi(t)>$ and where two-level state vectors are:

$$|\psi_j(t)> = C_{aj}(t)|a> + C_{bj}(t)|b>, \tag{3}$$

and so

$$\varrho = \Sigma_j P_j \begin{pmatrix} |C_{aj}|^2 & C_{aj}C^*_{bj} \\ C_{bj}C^*_{aj} & |C_{bj}|^2 \end{pmatrix}. \tag{4}$$

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[6] J. H. Eberly, "Toward a Theory of the Dye Laser," "Atomic and Molecular Optics," Proc. Rochester Symp., ed. by J. H. Eberly, Univ of Rochester (March 1971); also US Gov't Publication AD725218 (Defense Documentation Ctr), Alexandria, VA.

[10] M. Sargent III, M. O. Scully, and W. E. Lamb, Jr., "Laser Physics," Chaps 7, 14, and 16, Addison-Wesley, New York (1974).

[11] W. E. Lamb, Jr., Phys. Rev., *134* A1429 (1964).

The equation of motion, utilizing Schrodinger's time-dependent equation

$$\widehat{H}\,\psi(r,t) = i\hbar\,\frac{\partial\psi}{\partial t}\,(r,t) \tag{5}$$

is:

$$\dot{\varrho} = -\frac{i}{\hbar}\,[\widehat{H},\varrho]. \tag{6}$$

SS&L describe the use of the density matrix equations of motion in various aspects of laser quantum mechanical problems.[10]

SS&L showed that these matrix equations of motion could be used to derive equations for the Bloch model. In the Bloch model, a two-level system of magnetic dipoles of spin $\pm\,\tfrac{1}{2}$, is used to represent another two-level system (as a two-level laser system). This approach was used by Vahey and Yariv[8] for the singlet-triplet dye system. The Bloch equations are based upon the equations of motion through a magnetic field and include two relaxation terms of equations.[8] [10] [12]

Reservoir theory can be used with the density operator, $\varrho$, in laser calculations. The quantum mechanical treatment of dye lasers by Schaefer and Willis[9] combines reservoir theory with density matrices. As described by SS&L, the reservoir approach facilitates the division of a system into portions of primary (A) and secondary (B) interest. The "secondary" part becomes the reservoir, which can be eliminated by use of a "reduced density operator," $\varrho_{AB}(t)$.[10]

The "rotating wave approximation" has been used below.[6] [7] [9] This approximation allows one to eliminate terms where $(\omega + \nu)$ is in the denominator, or $e^{i(\omega + \nu)t}$ is present.[6] [10] Since $\omega$, the "matter" wave frequency in

$$\psi(r,t) = C_a\psi_a(r)\,e^{-i\omega_a t} + C_b\psi_b(r)\,e^{-i\omega_b t}. \tag{7}$$

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[6] J. H. Eberly, "Toward a Theory of the Dye Laser," "Atomic and Molecular Optics," Proc. Rochester Symp., ed. by J. H. Eberly, Univ of Rochester (March 1971); also US Gov't Publication AD725218 (Defense Documentation Ctr), Alexandria, VA.

[7] S. L. Chin and A. Zardecki, Phys. Rev. A, 13, 1528 (1976).

[8] D. W. Vahey and A. Yariv, Phys. Rev. A, 10 (6) 1578 (1974).

[9] R. B. Schaefer and C. R. Willis, Phys. Rev. A, 13 (5) 1874 (1976).

[10] M. Sargent III, M. O. Scully, and W. E. Lamb, Jr., "Laser Physics," Chaps 7, 14, and 16, Addison-Wesley, New York (1974).

[12] A. Yariv, "Quantum Electronics," Chap. 8, John Wiley and Sons, Inc., New York (1967).

and $\nu$, the "field" frequency of

$$E(t) \propto \cos(\nu t), \tag{8}$$

are equal under near resonance conditions, and $\omega >> 1$. $(\omega + \nu)$ is relatively large. For $e^{i(\omega + \nu)}$, rapid oscillation occurs, so that such terms average zero.[6]

In each of the discussions below, the symbolism as used by the authors, respectively, has been maintained in the section discussing their work. Kauzmann has discussed the fundamentals of the quantum mechanics of light interacting with matter and time-dependent processes.[13]

## II. APPLICATION OF THE LAMB LASER THEORY TO DYE LASERS

Eberly sought to derive a dye laser theory from the jointly interacting laser electric field and the polarization density of the dye.[6] He applied the Lamb laser theory to organic dye lasers, noting two important modifications would be necessary.[11] The dye laser must be treated as a four-level system at least, not a two-level one, and Lamb's use of the extreme Doppler limit would be inappropriate since dyes are conventionally used in solution. (One should note, however, that more recently lasing has been achieved with organic dye vapors.)[14][15]

The polarization density $P(t, z)$ was derived, based upon the Lamb theory, for dye molecules in the presence of the perturbing field $E(t, z)$. For a single mode of oscillation of an electromagnetic (light) wave in the laser cavity, given by $U(z)$, the natural frequency was $\Omega = \nu + \dot{\phi}$ (where $\phi(t)$ is the function describing the slow variation of $\phi$ with time, and $\nu$ is the frequency of the light wave.)

Further, assumptions were made that discrete modes were present in the laser cavity, that the vector nature of the field could be ignored (as well as its polarization), and that all parameters are functions of time, t, and cavity axial position, z, only. For the perturbing electric field,

$$E(t, z) = U(z) \epsilon (t) \cos (\nu t + \phi(t)).$$

[6] J. H. Eberly, "Toward a Theory of the Dye Laser," "Atomic and Molecular Optics," Proc. Rochester Symp., ed. by J. H. Eberly, Univ of Rochester (March 1971); also US Gov't Publication AD725218 (Defense Documentation Ctr), Alexandria, VA.

[11] W. E. Lamb, Jr., Phys. Rev., 134 A1429 (1964).

[13] W. Kauzmann, "Quantum Chemistry," Part V, Academic Press, New York (1957).

[14] P. W. Smith, P. F. Liao, et al., Appl. Phys. Ltrs., 25 144 (1974).

[15] B. Steyer and F. P. Schaefer, Opt. Comm., 10 219 (1974).

Here $\epsilon$ is the amplitude and is assumed to vary slowly with time. Only the first derivatives of $\epsilon(t)$ and $\phi(t)$ were used in Eberly's derivation. Since both $\phi(t)$ and $\epsilon(t)$ have been assumed to exhibit little change with time, this must be true for $E(t, z)$ also, so that the treatment is semiclassical.

The time-dependent projection of the polarization density $P(t, z)$ can be written as a function composed of oscillations in and out of phase with $\cos(\nu t + \phi(t))$ of $E(t, z)$:

$$P(t) = \int_{cavity} dz \, U(z) \, P(t, z)$$

$$= C(t) \cos(\nu t + \phi) + S(t) \sin(\nu t + \phi). \tag{9}$$

Using Maxwell's wave equation modified with an arbitrary conductivity constant $\sigma$ as a cavity loss correction factor, coupled differential equations for $\epsilon(t)$ and $\phi(t)$ were obtained (where $\eta$ is an arbitrary constant undefined further by Eberly):

$$(\nu + \dot{\phi} - \Omega) \, \epsilon(t) = -\tfrac{1}{2} \, (\nu/\eta^2)C(t) \tag{10}$$

$$\dot{\epsilon}(t) + \tfrac{1}{2} \, (\sigma/\eta^2) \, \epsilon(t) = -\tfrac{1}{2}(\nu/\eta^2) \, S(t). \tag{11}$$

These two equations, along with that for the polarization density, $P(t, z)$, are those equations subject to self-consistent (field) solution in Eberly's theory.

Eberly determined the polarization density according to Lamb's laser theory but adapted it to the unique characteristics of a dye system. The optical transitions involved in a lasing dye are shown in Figure 1. The assumptions basic to Eberly's treatment are:

a.  None but optical transitions contribute to the polarization density, and

b.  $P^2(t, z) = \sum_{t=i}^{n} p_i^2(t_i, z)$ (12)

where $n = 3$ in the present case and $p_i$ is the partial polarization associated with the i'th optical transition.

Addressing oneself to *one* of the transitions involved in the above summation, where $n = $ (level B — level a), and specifying $\lambda_B(t) = $ rate-time$^{-1}$-volume$^{-1}$ for the excitation of molecules into level/state "B." $P_i(t)$ becomes $P_B(t)$ or

$$P_B(t) = \int_{-\infty}^{t} dt_o \, \lambda_B(t_o) \, \bar{\mu}_B(t, t_o). \tag{13}$$

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For the dye molecules undergoing the transition B-a, there will be more than one final state possible, as noted above, so that:

$$\bar{\mu}(t, t_o) = \sum_a (\mu_{Ba} \varrho_{aB}^B + \varrho_{Ba}^B \mu_{aB}).$$  (14)

where $\mu_{Ba}$ and $\mu_{aB}$ are the dipole moments corresponding to the different final states. $\bar{\mu}_B(t, t_o)$ is the average or expectation value of $\mu_{molecule}$ in state B at time $t_B$ and $\varrho^B$ is the density matrix of that same molecule.[6][11]

$$\varrho^B = \begin{pmatrix} |B|^2 & Ba^* \\ B^*a & |a|^2 \end{pmatrix} = \begin{pmatrix} \varrho_{BB}^B & \varrho_{Ba}^B \\ \varrho_{aB}^B & \varrho_{aa}^B \end{pmatrix}$$  (15)

From the equation of motion for this density matrix,

$$i\bar{h}\dot{\varrho} = [H, \varrho] + \frac{\bar{h}}{2}(\gamma\varrho + \varrho\gamma),$$  (16)

$\gamma$ being the diagonal matrix:[10]

$$\gamma = \begin{pmatrix} \gamma_B & 0 \\ 0 & \gamma_a \end{pmatrix}$$  (17)

where $\gamma_B$ and $\gamma_a$ are the radiative decay constants for states B and a, and following the development of Eberly and Lamb, and invoking the rotating wave approximation, the polarization density for the B—a optical transition will be:[6][11]

$$P_B(t, z) = \frac{\lambda_B(t)}{2\gamma_D} \sum_a \left(-\frac{i}{h}\right) \frac{\mu_{Ba} \mu_{aB}}{\gamma_{Ba} + i(\omega_{Ba} - \nu)} U(z) \epsilon(t)e^{-i(\nu t + \phi)}$$  (18)

+ complex conjugate.

[6] J. H. Eberly, "Toward a Theory of the Dye Laser," "Atomic and Molecular Optics," Proc. Rochester Symp., ed. by J. H. Eberly, Univ of Rochester (March 1971); also US Gov't Publication AD725218 (Defense Documentation Ctr), Alexandria, VA.

[10] M. Sargent III, M. O. Scully, and W. E. Lamb, Jr., "Laser Physics," Chaps 7, 14, and 16, Addison-Wesley, New York (1974).

[11] W. E. Lamb, Jr., Phys. Rev., *134* A1429 (1964).

Expressions for $C_B(t)$ and $S_B(t)$ were obtained by Eberly from the P(t) equation (9):

$$C_B(t) = \frac{\eta^2}{\nu}\left(\frac{\lambda_B}{\gamma_B}\right) \beta \, \epsilon(t) \qquad (19)$$

$$S_B(t) = \frac{\eta^2}{\nu}\left(\frac{\lambda_B}{\gamma_B}\right) \alpha \, \epsilon(t), \qquad (20)$$

where

$$\alpha + i\,\beta = \int_\pi \frac{M_{Ba} D_a\,(\omega_{Ba})\,d\,\omega_{Ba}}{\gamma_{Ba} + i(\omega_{Ba} - \nu)} \qquad (21)$$

here, $M = 1$, since restricted to single mode, and $D_a(\omega_{Ba}) =$ energy density of state a with energy $\hbar\omega_{Ba}$.

Eberly obtained one last significant result from the theory outlined above, for the zero order. Using the above expressions for $C_B(t)$ and $S_B(t)$, the photon gain from the B $\leftarrow$ a transitions, $G_{B \leftarrow a}$ is:

$$G_{B \leftarrow a} = (2\dot{\epsilon}/\epsilon)_{B \leftarrow a} = \frac{\nu}{\eta^2}\ S_B(t)/\epsilon(t) \qquad (22)$$

$$= \left(\frac{\lambda_B}{\gamma_B}\right) \frac{\gamma_{Ba}}{\pi} \int \frac{M_{Ba}\, D_a\,(\omega)\,d\,\omega}{[(\omega - \nu)^2 + \gamma_{Ba}^2]}. \qquad (23)$$

This expression was similar to one Eberly had obtained earlier using rate equations and applied to problems associated with the threshold for organic dye lasers.[6][16]

[6] J. H. Eberly, "Toward a Theory of the Dye Laser," "Atomic and Molecular Optics," Proc. Rochester Symp., ed. by J. H. Eberly, Univ of Rochester (March 1971); also US Gov't Publication AD725218 (Defense Documentation Ctr), Alexandria, VA.

[16] O. G. Peterson, J. P. Webb, W. C. McColgin, and J. H. Eberly, J. Appl. Phys., 42 (5) 1917 (1971).

## III. PROPAGATION OF LIGHT PULSES

The semiclassical self-consistent approach was also used by Chin and Zardecki to describe the propagation of light pulse through a dye medium and also the superposition of short light pulses in that medium.[7] A multi-level model for a dye molecule in solution was presented. Triplet states are ignored since the duration of the pulse trains is too short for intersystem crossing to occur. Essentially, the "supermolecule" (the dye molecule in its solvent cage) when perturbed by the absorption of a light pulse undergoes several transitions (A→b, b→B, B→a, and a→A of Figure 1) between equilibrium (A and B of Figure 1) and non-equilibrium states (b and a of Figure 1).

Equations of motion were derived using a population matrix formulation, $\varrho(z, t)$, for the interaction of the radiation field and the dye "supermolecules." A basic assumption is made that:

$$\gamma_{ab}^{-1} << T_p << \gamma_x^{-1},$$  (24)

where $T_p$ is the pulse duration, $\gamma_{ab}^{-1}$ is the atomic memory time, and $\gamma_x^{-1}$ is the non-radiative decay time from b to B in Figure 1. The field is regarded as a linearly polarized running wave for which the amplitude and phase vary slowly. The amplitude envelope function, $\xi$, used was:

$$\frac{\partial \xi}{\partial z} + \frac{1}{c} \frac{\partial \xi}{\partial t} = -\kappa\xi - \frac{1}{2\epsilon_0} k S_{AB},$$  (25)

where $k = \dfrac{\omega_L}{c} = \dfrac{\text{mean frequency of incident pulse}}{\text{velocity of light}}$, $\kappa$ represents nonresonant losses in the medium, and $\epsilon_0$ is the vacuum permittivity. $S_{AB}$ is the quadrature component of the total polarization, $P_{AB}$, and is computed using the rotating wave approximation. The phase function, $\phi$, for the electric field is:

$$\phi = \omega_L t - kz + \phi (z, t).$$  (26)

As in Eberly's treatment, a perturbation method was used, the perturbation being $\dfrac{\mu E}{\hbar}$ where $\mu$ is the dipole matrix element between states and E is the energy of the transition. Expressions for the perturbed and unperturbed Hamiltonians were given to be used in generating the equations of motion.

[7] S. L. Chin and A. Zardecki, Phys. Rev. A, *13*, 1528 (1976).

The total polarization $P_{AB}$ can be expressed as the sum of the partial polarizations, $P_{ab}$:

$$P_{AB} = \sum_a \sum_b P_{ab} \tag{27}$$

$$= C_{AB}(z, t)\cos \phi + S_{AB}(z, t)\sin \phi. \tag{28}$$

$$P_{ab}(z, t) = \mu_{ba}\, \varrho_{ab}(z, t) + \mu_{ab}\, \varrho_{ab}(z, t). \tag{29}$$

The population maxtrix used to express the equations of motion for the "supermolecule" in any of the states, $\alpha$, in levels A or B was:

$$\varrho(z, t) = \sum_\alpha \int_{-\infty}^t dt_0 \lambda_\alpha(z, t_0)\, \varrho(\alpha, z, t_0, t). \tag{30}$$

Here, $p(\alpha, z, t_0 t)$ is the density matrix for a molecule (at place z, time $t_0$) in state $\alpha$, and $\lambda_\alpha$ $(z, t_0)$ is the molecular concentration per unit time in state $\alpha$. Four equations of motion,
$\dot{\varrho} = \dfrac{-i}{\hbar} (\widehat{H}, \varrho)$, were given, $\dot{\varrho}_{aa}$, $\dot{\varrho}_{bb}$, $\dot{\varrho}_{ba}$, and $\dot{\varrho}_{ab}$. Using zeroth order elements of the population matrix, Chin and Zardecki define the population difference in a and b, $N_{ba}^{(o)}$:

$$N_{ba}^{(o)} = \varrho_{bb}^{(o)} - \varrho_{aa}^{(o)}. \tag{31}$$

If the photon flux is defined as $I = \dfrac{\epsilon_0 \xi^2 c}{2\hbar \omega_L}$, and $I_0$ is the input pulse at $z = 0$, then the flux modified by multiple transitions is:

$$I(z, t) = \frac{I_0 (t - z/c)\, e^{(a_1 - 2\kappa)z}}{1 - [a_2/(a_1 - 2\kappa)]\, I_0(t - z/c) \left\{1 - e^{[(a_1 - 2\kappa)z]}\right\}} \tag{32}$$

Resonant absorption to the first and second order in the photon flux is given by the coefficients $a_1$ and $a_2$.

Chin and Zardecki applied their theory to the spectral hole burning phenomena, obtaining results consistent with those of Mouro[17] for dye molecules in a solvent cage. They also addressed the case of two adjacent pulses being superposed in a dye medium. The first pulse obeys the condition of equation (24). The second pulse is similar to the first and occurs after a time delay, T. This delay is much shorter than the fluorescence time of the dye molecule in level B and is much shorter than the solvent-solute relaxation time. As in the propagation study, equations of motion were derived for the time evolution of the population matrix elements, and expressions for the photon flux were found. The pulse superposition effect is defined by the authors as the storage of the energy of a first pulse as a population inversion, and stimulated emission occurring subsequently upon irradiation with a second pulse. Their derivation involved separating the absorption and amplification processes, so that in the direct-transition approximation the photon flux becomes:

$$\frac{\partial I}{\partial z} + \frac{1}{c}\frac{\partial I}{\partial t} = \left[ \varrho_{BB}(T) \sum_{d} \sigma_{Bd} - 2\kappa - \sum_{a,b} \sigma_{ba} \varrho_{aa}^{(o)} \left( 1 + \frac{2\sigma_{ba}}{\widehat{\gamma}_{ba}} I \right)^{-1} \right] I. \quad (33)$$

Qualitative experimental support for the superposition theory was presented using oxazine perchlorate in glycerine.

## IV. SPECTRAL CROSS-RELAXATION AND COLLISIONAL DEPHASING EFFECTS

That the absorption of light by organic dye molecules is far from a simple process was shown in the semiclassical theory of Vahey and Yariv.[8] They treated dye solutions interacting with light at high-incident flux, as an ensemble of optical dipoles. Absorption of light in this case may exhibit inhomogeneous broadening or absorption occurring for the ensemble over a wider frequency band than would be anticipated for a lone optical dipole.[8,10] Spectral cross-relaxation results when the configuration of the solvent cage or environment surrounding the optical dipole-dye molecule is altered in some way. Another effect which may occur during the interaction of light and an optical dipole-dye molecule, is that of a random shift in the phase of the radiating dipole due to collisions in the dye system.[8,10]

[8] D. W. Vahey and A. Yariv, Phys. Rev. A, 10 (6) 1578 (1974).

[10] M. Sargent III, M. O. Scully, and W. E. Lamb, Jr., "Laser Physics," Chaps 7, 14, and 16, Addison-Wesley, New York (1974).

[17] G. Mouro, IEEE J. Quantum Electron., QE-11 (1) 1 (1975).

Vahey and Yariv point out that earlier treatments of the interaction between light and matter have included neither spectral cross-relaxation effects nor collisional dephasing. They presented a semiclassical study which did consider these effects.[8] Application of their theory to experimental data for certain well-known cyanine saturable absorber dyes accounted for observed "hole-burning" in the absorption spectrum due to cross-relaxation (see Figure 3 of Mouro[17]). They determined that if:

$T_1$ = time constant for deactivation or decay or excited molecules

$T_2$ = time constant for collisional dephasing

$T_3$ = time constant for spectral cross-relaxation (and if $T_A$ = time constant for absorption, and $\frac{1}{T} \propto$ rate of optical process), then distortion in the absorption spectrum will occur when $\frac{1}{T_A} > \frac{1}{T_3}$, and coherent interaction effects will be significant

when $\frac{1}{T_A} \sim \frac{1}{T_2}$. Vahey and Yariv are concerned here with systems in which

$T_2 \leq \frac{1}{10} T_1$. Rate equations were derived by Vahey and Yariv, based upon concepts evolving from likening the dye absorbers to an ensemble of liquid-free spins interacting with radiation. The Bloch equations were applied to such systems, affording a vector model of the density matrix equations of motion.[8] [10] [12] The model used was that of a single dye molecule (state vector $(u', v', r')$) which underwent only one collision, a strong collision, at time $t_0$. The undamped Bloch equation,

$$\vec{dr}/dt = \vec{\omega} \times \vec{r}'$$ (34)

was applied to the molecule with the conditions that:

$$\vec{r}' (t = t_0) = (0,0,\pm 1); \vec{r}'(t) = (u', v', r')$$

$$\vec{\omega} = (\omega_1(x, t), 0, \omega_0 - \omega + \delta(t))$$

$(\omega_0 - \omega)$ is the detuning frequency,

$\omega_1$ = a frequency proportional to the field amplitude,

$\delta(t)$ = the temporal detuning generated by cross-relaxation.

[8] D. W. Vahey and A. Yariv, Phys. Rev. A, 10 (6) 1578 (1974).

[10] M. Sargent III, M. O. Scully, and W. E. Lamb, Jr., "Laser Physics," Chaps 7, 14, and 16, Addison-Wesley, New York (1974).

[12] A. Yariv, "Quantum Electronics," Chap. 8, John Wiley and Sons, Inc., New York (1967).

[17] G. Mouro, IEEE J. Quantum Electron., QE-11 (1) 1 (1975).

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A solution of the Bloch equation is $v'(\omega_1, \omega_o -\omega, t\text{-}t_o, \pm 1)$. Since the undamped equation was used, Vahey and Yariv note that $u'$, $v'$, and $r'$ are not ensemble averages, but are averages determined by a summation of microscopic state vectors produced since times $t_o$ by random collisions at interval $T_2$.

Using this model to address the question of optical absorption in dye molecules, where $\vec{p}(x, t, \omega_o)$ is the induced dipole moment (due to a polarized field, $\vec{E}(x, t)$) and $\vec{p}_o$ is the dipole matrix element due to the initial and final states, the authors obtain:

$$\vec{p}(x, t, \omega_o) = \vec{p}_o[-u(x, t, \omega_o)\cos(\omega\,t\text{-}kx) + v(x, t, \omega_o)\sin(\omega t\text{-}kx)] \tag{35}$$

since

$$\vec{E}(x, t) = \hat{e}_z\,\xi\,(x, t)\cos(\omega\,t\text{-}kx). \tag{36}$$

The out-of-phase component of polarization, $v(x, t, \omega_o)$, is:

$$v(x, t, \omega_o) = \int_{-\infty}^{t} \frac{dt_o}{T_2}\ e^{-(t-t_0)/T_2}\ [n_b(x, t_o+, \omega_o)\,v'(\omega_1, \omega, t - t_o - 1)$$
$$+ n_a(x, t_o+, \omega_o)\,v'(\omega_1, \omega_o - \omega, t - t_o + 1)]. \tag{37}$$

This is the instantaneous polarization. The probability that the dye ground state remained occupied after collision occurred (at time $t_o$) was given by $n_b(x, t_o +, \omega_o)$. The probability that dye molecules would be found in an excited state at time $(t_o +)$ was $n_a(x, t_o +, \omega_o)$; to eliminate systems showing stimulated emissions, $n_a = 0$. Development of an expression for $n_b(x, t_o +, \omega_o)$ leads to expressions for the induced polarization:

$$v(x, t, \omega_o) = \frac{\omega_1(x, t)\,T_2}{1 + \omega_1^2\,(x, t)\,T_2^2 + (\omega_o - \omega)^2\,T_2^2}\ \left\{ n_b(x, t, \omega_o)[1 - (T_2/T_3)] \right. \tag{38}$$

$$\left. + \int_{-\infty}^{\infty} d\,\omega_o'\,g(\omega_o' - \bar{\omega}_o)\,m_b(x, t, \omega_o')(T_2/T_3) + n_c(x, t)(T_2/T_1) \right\}$$

In phase $u(x, t, \omega_o)$:

$$u(x, t, \omega_o) = -(\omega_o - \omega(\,T_2 v(x, t, \omega_o). \tag{39}$$

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To relate the induced polarization and light absorption, the electromagnetic wave equation was separated into two equations, one for phase and one for amplitude. The wave amplitude, $\xi(x, t)$ is

$$\frac{\partial \xi}{\partial x} + \frac{n_o}{c} \frac{\partial \xi}{\partial t} = -\tfrac{1}{2} N_o \frac{\omega P_o}{\epsilon_o n_o c} \int_{-\infty}^{\infty} d\omega_o g(\omega_o - \bar{\omega}_o) v(x, t, \omega_o). \qquad (40)$$

Here, $N_o$ is the absorber concentration, while the refractive index of the solvent is given by $n_o$. One of the basic consequences obtained by Vahey and Yariv, the photon-transport equation, evolved from the wave amplitude equation. The transport equation is:

$$\left(\frac{\partial}{\partial x} + \frac{n_o}{c} \frac{\partial}{\partial t}\right) F(x, t) = -N_o \sigma_h F(x, t) < n_{eff}(x, t, \omega_o) \; \mathcal{L} \; (F, \omega_o - \omega) > \text{av.}, \quad (41)$$

where the flux density is:

$$F(x, t) \cong \tfrac{1}{2} \epsilon_o cn_o \, \xi^2(x, t)/\hbar\omega, \qquad (42)$$

the homogeneous cross section for interaction of molecules in exact resonance with the wave is

$$\sigma_h = \omega p_o^2 \, T_2 / \epsilon_o cn_o \hbar, \qquad (43)$$

The effective ground-state population is

$$n_{eff}(x, t, \omega_o) = n_b(x, t, \omega_o)[1 - (T_2/T_3)]$$
$$+ \; < n_b(x, t, \omega_o) >_{av} \; (T_2/T_3) \qquad (44)$$

and $\mathcal{L} \; (F, \omega_o - \omega)$ is a modified Lorentzian function.

The other significant theoretical result obtained was the population rate equation:

$$\frac{\partial}{\partial t} \, n_b(x, t, \omega_o) = -\sigma_n F(x, t) \, n_{eff} (x, t, \omega_o) \, \mathcal{L}(F, \omega_o - \omega) -$$

$$\left\{ [n_b(x, t, \omega_o) - < n_b(x, t, \omega_o) > \text{av}]/T_3 \right\} + n_c(x, t)T_1 . \qquad (45)$$

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Vahey and Yariv applied their theory to two classes of absorbers, according to:

(1) Steady-state limit, where the pulse duration is long with respect to $T_1$ and $T_2$.

(2) Short-pulse limit, where the pulse duration is very short compared to $T_1$ and $T_2$.

For the steady-state case, they found that the experimental parameter in giant-pulse studies with organic dyes is the steady-state transmission:

$$\frac{F(x)}{F(0)} = \frac{Q^2(x) - 1}{Q^2(0) - 1} \tag{46}$$

where

$$Q = [1 + F\sigma_h(T_2 + T_3)]^{1/2} \tag{47}$$

and $F(0)$ is a known input flux density. In the short-pulse case, the theory was extended to such problems occurring in real-world absorbing systems as:

(a) Excited state absorption.

(b) The molecular anisotropy dependence.

(c) The multiplicity of interacting excited states.

## V. A QUANTUM-MECHANICAL DYE LASER THEORY INVOLVING EXACT TREATMENT OF TRIPLET STATES

Schaefer and Willis were the first to present a dye laser theory which was not only fully quantum-mechanical, including radiation fluctuations, but also treated the triple states exactly.[9] As noted above, dye lasers are unique among lasers because both singlet and triplet levels can be populated during lasing.

The model upon which this quantum-mechanical treatment was based, consisted of two main parts—matter and radiation. Reservoir theory was invoked, creating a matter or molecule reservoir (singlet and triplet level decay) and a radiation reservoir (accounting for radiative losses in the laser cavity).[10]

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[9] R. B. Schaefer and C. R. Willis, Phys. Rev. A, *13* (5) 1874 (1976).

[10] M. Sargent III, M. O. Scully, and W. E. Lamb, Jr., "Laser Physics," Chaps 7, 14, and 16. Addison-Wesley, New York (1974).

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The Hamiltonian, $\widehat{H}$, for this model became:

$$\widehat{H} = [\widehat{H}_R + \widehat{H}_M + V_{R-M}] + [\widehat{H}_{R-res} + V_{R-res}] + [\widehat{H}_{M-res} + V_{M-res}]. \qquad (48)$$

where V represents the intersection Hamiltonian potential. The terms are defined by Schaefer and Willis as:

$\widehat{H}_R$ = radiation Hamiltonian

$\widehat{H}_M$ = molecule Hamiltonian

$\widehat{H}_{R-res}$ = radiation-reservoir Hamiltonian

$\widehat{H}_{M-res}$ = molecule-reservoir Hamiltonian

$V_{R-M}$ = radiation-molecule interaction

$V_{R-res}$ = radiation-radiation reservoir interaction

$V_{M-res}$ = molecule-molecule reservoir interaction.

The reservoir terms were eliminated in Schaefer and Willis because the only reservoir attributes of interest were those of pumping and decay and not specific details about the reservoirs.

The radiation field Hamiltonian was:[9]

$$\widehat{H} = \sum_{\vec{k}} \sum_{\alpha} \hbar \, \Omega_k \, (a^{\dagger}_{\vec{k},\alpha} \, a_{\vec{k},\alpha} + \tfrac{1}{2}) \qquad (49)$$

where $\sum_{\vec{k}}$ represents summation over all cavity modes (in the present case $\vec{k} = 1$, since only a single-mode was treated), and $\sum_{\alpha}$ represents summation overall $\alpha$ polarizations. The frequency associated with $\vec{k}$ is $\Omega_k$. The "a and $a^{\dagger}$" operators are annihilation and creation photon operators, respectively.[10]

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[9] R. B. Schaefer and C. R. Willis, Phys. Rev. A, *13* (5) 1874 (1976).

[10] M. Sargent III, M. O. Scully, and W. E. Lamb, Jr., "Laser Physics," Chaps 7, 14, and 16, Addison-Wesley, New York (1974).

Turning to the Hamiltonian for matter, $\widehat{H}_M$, the singlet-triplet states associated with dye molecule energy levels require that:

$$\widehat{H}_M = \widehat{H}_S + \widehat{H}_T \tag{50}$$

where

$$\widehat{H}_S = \sum_\sigma \sum_i (s_{\sigma,i}^\dagger s_{\sigma,i} \epsilon_i)$$

$$\widehat{H}_T = \sum_\sigma \sum_j (t_{\sigma,j}^\dagger t_{\sigma,j} \epsilon_j)$$

and  $\sigma$  =  total dye-molecules active in laser system

$\quad\quad$ i  =  singlet states

$\quad\quad$ j  =  triplet states

$\quad\quad \epsilon_i$ & $\epsilon_j$  =  energies corresponding to i or j levels, respectively

$\quad s_{\sigma,i}^\dagger$ & $t_{\sigma,j}^\dagger$  =  creation operators for singlets, triplets, respectively

$\quad s_{\sigma,i}$ & $t_{\sigma,j}$  =  annihilation operators for singlets and triplets, respectively.

The relationship between the molecular annihilation and creation operators were given:

$$[s_{\sigma,i}^\dagger, s_{\sigma,j} = \delta_{ij}] \quad\quad [t_{\sigma,i}^\dagger, t_{\sigma,j} = \delta_{ij}] \tag{51}$$

$$[s_{\sigma,i}^\dagger, s_{\sigma,j}^\dagger] = [s_{\sigma,i}, s_{\sigma,j}] = [t_{\sigma,i}^\dagger, t_{\sigma,j}^\dagger] = [t_{\sigma,i}, t_{\sigma,j}] = 0 \tag{52}$$

$$[s_{\sigma,i}^\dagger, t_{\sigma,j}^\dagger] = [s_{\sigma,i}^\dagger, t_{\sigma,j}] = [s_{\sigma,i}, t_{\sigma,j}^\dagger] = [s_{\sigma,i}, t_{\sigma,j}] = 0 \tag{53}$$

That the molecule or matter terms must be treated as singlets and triplets was shown also in the radiation-matter interaction Hamiltonians:

$$V_{R-M} = V_{R-S} + V_{R-T}. \tag{54}$$

From the matter-radiation interaction (dipole approximation), Schaefer and Willis found:

$$\tag{55}$$

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$$V_{R\text{-}S} = i \sum_{\sigma} \sum_{i,j} \sum_{k} \gamma_{\sigma ijk} (s_{\sigma,i}^{\dagger} s_{\sigma,j} a_k^{\dagger} + s_{\sigma,j}^{\dagger} s_{\sigma,i} a_k), \qquad (55)$$

where $\epsilon_j > \epsilon_i$,

$$\gamma_{\sigma ijk} = [4 \pi e^2 (\epsilon_j - \epsilon_i)^2 \, h \Omega_k \, V]^{\frac{1}{2}} \times (\vec{\epsilon} \cdot \vec{\chi}) \, \Gamma (\chi);$$

$$V_{R\text{-}T} = i \sum_{\sigma} \sum_{1,m} \sum_{k} \gamma_{\sigma 1mk} (t_{\sigma,1}^{\dagger} t_{\sigma,m} a_k^{\dagger} + t_{\sigma,m}^{\dagger} t_{\sigma,1} a_k) \qquad (56)$$

where $\epsilon_1 > \epsilon_m$,

$$\gamma_{\sigma 1mk} = [4 \pi e^2 (\epsilon_m - \epsilon_1)^2 \, h \, \Omega_k \, V]^{\frac{1}{2}} \times (\chi_{1m}) \, \Gamma (\chi).$$

$m = $ electron mass

$\chi_{1m} = $ dipole matrix element

$e = $ electronic charge

$V = $ volume of laser cavity

$\Gamma (\chi) = $ eigenfunction for the spacial cavity

$\sum_{ij}$ for $j > i$

$\sum_{1,m}$ for $m > 1$

$\sum_{k} = 1$ for single-mode operation.

The *rotating wave* approximation was applied to the interaction Hamiltonians by the authors. (Thus transitions were eliminated where photon *absorption* might produce a *lower* energy level and photon *emission* might yield a *higher* energy level). Thus, from the commutation relations cited, $s^{\dagger} s a^{\dagger}$ (or $t^{\dagger} t a^{\dagger}$) terms correspond to the creation (emission) of a photon and decrease in molecular energy level. Similarly, $s^{\dagger} s a$ (or $t^{\dagger} t a$) terms indicate photon annihilation (absorption) and an increase in molecular energy levels.

Having defined the system Hamiltonian, Schaefer and Willis utilized the Born-Markoff[18] approximation for the Liouville equation.

$$\frac{d\hat{p}(t)}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{p}(t)], \hat{p}(t) \text{ being the density operator of the system} \qquad (57)$$

To demonstrate the validity of such an approach, they calculated that experimental data for Rhodamine 6G, one of the best-studied laser dyes, did indeed satisfy the criterion for validity that its (continuous-wave lasing) interaction time is minimal compared to the relaxation time, or $(t_{int}/t_{rel}) << 1$.

Thus,

$$0.025 \leqslant \left( \frac{SN}{\nu_{S,1}} \right) \leqslant 0.04 \qquad (58)$$

and

$$0.01 \leqslant \left( \frac{TN}{\nu_{T,u}} \right) \leqslant 0.03 \qquad (59)$$

where

N = number of lasing organic molecules

S = stimulated emission rate of singlets

T = stimulated absorption rate for triplets

$\nu_{S,1}$ = lower singlet decay rate

$\nu_{T,u}$ = upper triplet decay rate.

Clearly, both the singlet and triplet contributions satisfy the $(t_{int}/t_{rel}) << 1$ criterion.

---

[18] SS&L, in discussing the Markoff approximation, note that the average value of a random shift in an energy difference is zero, so that if the variations of this shift are rapid compared to other decay times (relaxation times) in the system, then, $\dfrac{\text{(average shift)}}{\text{decay time}} \sim 0$.

If $\hat{H} = \hat{H}_o + \lambda V$ and $\lambda$ is dimensionless, the above approximation was given as:

$$\frac{d\hat{p}(t)}{dt} + \frac{i}{h} [\hat{H}_o, \hat{p}(t)] = -\lambda^2 \int_o^\infty dT[V, (V(T), \hat{p})], \tag{60}$$

where $V(T) = e^{i\hat{H}_o T/h} V e^{-i\hat{H}_o T/h}$. \tag{61}

This equation was shown by Willis to describe laser photon statistics if one does not separate matter-radiation interactions into factorable matrices.[19]

Equations of motion were derived next. As derived by Schaeffer and Willis, using the Born approximation master equation where the diagonal matrix is coupled only to the diagonal elements, two matrices result:

### Radiation Density Matrix

$$R_n = <n|R|n> \tag{62}$$

### Diagonal Single-particle Radiation Density Matrix

$$D_n^j(t) \equiv <n|<j| D(1, t) |j>|n>; \tag{63}$$

here n is the photon number, and j refers to the state of the jth molecule. Two sets of equations of motion were formulated from these matrices. One set, the equation of motion for the radiation density operator $\hat{R}(t)$ is:

$$\frac{d R_n(t)}{dt} = \nu_R[n \overset{①}{R_n} - (n + 1) \overset{②}{R_{n+1}}]$$

$$- S N [(n + 1) (D_n^{S,u} \overset{③}{-} D_{n-1}^{S,\varrho}) + n(D_n^{S,\varrho} \overset{④}{-} D_{n-1}^{S,u})] \tag{64}$$

$$- T N [(n + 1) (D_n^{T,u} \overset{⑤}{-} D_{n+1}^{T,\varrho}) + n(D_n^{T,\varrho} \overset{⑥}{-} D_{n-1}^{T,u})].$$

---

[19] C. R. Willis. Phys. Rev., *165* 420 (1968).

The terms labeled ① and ② give the radiation decay associated with the radiation reservoir, ③ is emission (stimulated and spontaneous) in the singlet state, ④ is stimulated absorption for the ground singlet state, and ⑤ and ⑥ are the terms corresponding to ③ and ④ respectively, for the triplet state. The other set for the singlet-molecule-radiation density operator $\widehat{D}(\ell, t)$ was composed of four equations to satisfy the possibility that the molecule could be in a single (S) or triplet (T) state, and in an upper (u) or lower ($\ell$) level of state:

$$\frac{dD_n^{S,u}(t)}{dt} = -(\nu_{S,u} + K_{ST})\, D_n^{S,u} + R_n(t)\, \nu_e - S(n+1)\,(D_n^{S,u} - D_{n+1}^{S,\ell}), \qquad (65)$$

$$\frac{dD_n^{S,\ell}(t)}{dt} = -\nu_{S,\ell}\, D_n^{S,\ell} - S_n\,(D_n^{S,\ell} - D_{n+1}^{S,u})\,(n+1) \qquad (66)$$

$$\frac{dD_n^{T,u}(t)}{dt} = -\nu_{T,u}\, D^{T,u} - T(D_n^{T,u} - D_{n+1}^{T,\ell})\,(n+1) \qquad (67)$$

$$\frac{dD_n^{T,\ell}(t)}{dt} = K_{ST}\, D_n^{S,u} + \beta\nu_{T,u}\, D_{n-1}^{T,u} - \nu_\ell D_n^{T,\ell} - nT(D_n^{T,\ell} - D_{n-1}^{T,u}). \qquad (68)$$

These two sets of equations are the fundamental ones for the Schaefer-Willis dye laser theory. Several solutions were obtained, incorporating the parameters $\alpha$ and $\beta$:

$\alpha$ = a triplet parameter:

the value of $\alpha$ increases with triplet concentration.

$$\alpha \equiv (T\, K_{ST}/S\, \nu_{T,\ell}).$$

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$\beta$, where $0 \leq \beta \leq 1$, and

where

$T$ = triplet stimulated absorption rate

$S$ = singlet stimulated emission rate

$K_{ST}$ = intersystem crossing rate

$\beta$ = fraction return of excited triplets, $0 \leq \beta \leq 1$

$V_e$ = molecular excitation rate due to external pump

$n$ = number of photons

$V_R$ = radiation decay rate.

The dye laser exact solution for the steady state was obtained:

$$R_{n+1} = \Pi_{p=0}^{n} \; G(p) \, R_0 \qquad (69)$$

where $\quad G(p) \equiv \left( \dfrac{S\eta_p^{S,u} + T\eta_p^{T,u}}{S\eta_{p+1}^{S,\ell} + T\eta_{p+1}^{T,\ell} + \nu_R / N} \right)$

$p$ is an integer.

$\Pi_{p=0}^{n}$ is the product of terms for $0 \leq p \leq n$.

and $\eta_n^{S,u}$ is obtained from $D_n^{S,\ell}(t) = \eta_n^{S,\ell}(t) \, R_n(t)$ when

$$\frac{dD_n^{S,u}(t)}{dt} = Q \text{ in equations (65) } - \text{ (68)}.$$

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Simplified solutions of this equation were obtained by (1) eliminating the triplets, giving the "singlet-state case," and (2) including the triplets, but neglecting terms for triplet-state emission and singlet-state absorption to obtain the "approximate solution." Finally, graphical solutions of the exact equation were obtained by computer methods.

Results of the various solutions were expressed as the extrema of $R_n$, the threshold value of pumping, and variations in $R_n$ when pumping values are above threshold. One interesting result of this theory is that, instead of one (maximum) extremum for the radiation distribution, $R_n$, as is found for a gas laser, for the dye laser it is possible to expect both a maximum and a minimum for $R_n$, depending upon other laser parameters.

## VI. CONCLUSIONS

The basic quantum mechanical studies of dye lasers have been reviewed. Despite the complexity of dye laser systems, compared to other laser systems, successful results have been achieved. An acceptable understanding exists of dye lasers and their potential prospects in the areas of spectral hole burning, gain, propagation of light pulses in the dye medium (and the superposition of two light pulses), light absorption and emission processes for states of different multiplicities, and pumping thresholds. Although much remains to be done, these studies demonstrate the unique contribution quantum mechanics can make upon an examination of a time-dependent interaction of matter with the electrical field component of light in a dye medium.

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